Assessment Of Air Quality In The Southwestern Part Of The Świętokrzyskie Mountains Based On Selected Indicators

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Abstract

Background: This article presents the results of research on the air quality which has been under the anthropogenic impact of the cement and lime industry in the Świętokrzyskie Mountains for many years. Research using geo- and bio-indicators was carried out at fixed measuring points in the years 2016-2018.

Results: *Hypogymnia physodes* (L.) *Nyl.* and two-year old Scots pine needles *Pinus silvestris* L. were used for bioindication research. Physico-chemical properties of precipitation were developed on the basis of research conducted at the Jan Kochanowski University's field research station located on the Malik. Increased pH and specific electrolytic conductivity (EC) of precipitation, as well as variable concentrations of heavy metals throughout a year were shown.

Conslusions: Analysis of the chemical properties of transplanted lichens and pine needles confirmed the presence of elements from the cement and lime industry sector located in the Białe Zagłębie. Scanning electron microscope (SEM) image of the needles' surface revealed morphological changes resulting from pollution of stoma opening and closing by small solid particles of anthropogenic origins, disturbing a gas exchange.

Background

Gas and dust emissions from specialised industrial centres are the largest sources of anthropogenic pollutants to the atmosphere, soil and surface waters. It has a negative effect on the natural environment [1–9] and human health [10]. In this aspect, long-term deposition of trace elements contained in cement-lime dust, including heavy metals that are toxic to the environment (lead, chromium, nickel, cadmium), is particularly important. Poland is one of the leading producers of cement in Europe (17.3 million tons in 2017 - data from the Central Statistical Office of Poland 2017), taking the third place behind Germany and Italy. Lime production amounting to 1904 thousand tons (2017) gives Poland the fifth place. A significant part of these products is produce in plants located within the Białe Zagłębie in the Świętokrzyskie Mountains. The Białe Zagłębie consist of cement plants in Nowiny and Małogoszcz as well as lime plants in Bukowa and Trzuskawica. Almost fifty years of the functioning of the Białe Zagłębie have caused changes in the natural environment [11, 12, 13, 14]. This article determines the amount of metal deposition using the accumulation capacity of selected living organisms and atmospheric precipitation over the study area. Before, the issue of bioindication in industrialised areas was undertaken by Alaimo et. al. [15], Sawicka-Kapusta et al. [16], Ots and Mandre [17], Parzych et al. [18], and - when it comes to the Świętokrzyskie Region - by Migaszewski et al.[19], Jóźwiak [20], Barga – Więcławska and Świercz [21], as well as Kozłowski et al. [22], among others. The properties of atmospheric precipitation in areas exposed to anthropogenic impact were determined, among others, by Baciak et al.[23], Kasina [24], Sporek [25], Polkowska et al. [26], Stachnik et al.[27], Kozłowski et al. [28], as well as Jóźwiak [29] when it comes to the Białe Zagłębie. The combination of geo- and bio-indicators was used to develop a multi-factorial assessment of the natural environment and its transformation within the Białe Zagłębie. The interdisciplinary approach to research, combining geographical, biological and chemical research methods, allows for monitoring industrial impact on plants along with their technical infrastructure, roads, spoil tips and mining areas.

Materials And Methods

Currently, industrial scale operations concentrated within the Białe Zagłębie cover an area of about 180 km^2 in the south-western part of the Świętokrzyskie Mountains [30], forming an irregular triangle (Fig. 1). The largest plants producing cement and lime products are located in Bukowa, Małogoszcz, Trzuskawica and Nowiny. Mass production and significant fuel consumption in the technological process result in increased emissions of harmful gases and dust into the atmosphere (Fig. 2). Despite modernisation and innovation activities over the last decades [31, 32], their presence is a basic factor reducing the quality of air in this part of the region [33]. Monitoring carried out in 2016–2018 was aimed at determining the range of impact of cement and lime plants as well as a multi-factorial assessment of the state of natural environment under the influence of such kind of emission. The measuring system included tests conducted on permanent control surfaces where lichen transplantation, pine needle collection and precipitation sampling were carried out (Fig. 1).

Due to good bioindication properties, two-year-old needles of Scots pine Pinus silvestris L., forming dense complexes of upland and lowland forests with rich undergrowths and lower fir floors, were selected for monitoring analyses. Within the calciphilic Białe Zagłębie, there is no presence of Hypogymnia physodes (L.) Nyl used in bioindication [34, 35, 36, 37, 38], and that is why, it was transplanted from the Borecka Primeval Forest (north-eastern Poland) where it occurs widely. The Borecka Primeval Forest belongs to the most valuable forest complexes in Europe due to the natural preservation of Central European deciduous forest habitats and the low anthropogenic impact characterised by a negligible share of heavy metal concentrations in atmospheric precipitation [39]. The Hypogymnia physodes (L.) Nyl lichens were taken on approx. 30-cm twigs and then placed in 22 control points at a height of approx. 2 m above ground level, using plastic self-locking bands. The duration of lichen exposure in the area of anthropogenic pressure lasted for six months in four measuring series, two for each half year (warm, cool). Each time, lichens (after the transplantation time) and pine needles (after the growing season) were transported to the Environmental Research Laboratory of the Jan Kochanowski University, where they were subjected to further tests. All samples were washed with deionised water three times. After having been dried at $65^{0}C$ for 24 hours, the air-dried samples were ground in an IKA A-11 Basic organic matter mill. In the ground samples, pH was analysed in solutions obtained by mixing the samples with water or a 1N KCl purum p.a. solution in a ratio of 1:2.5. After 24 hours, the pH value was measured using a HACH HQ-40d multiparameter with an INTELLICAL electrode. A mixture of nitric acid (V) (Suprapur Merck 65%) and hydrogen peroxide purum p.a. in a ratio of 2.5:1 was used for distributing wet samples of 0.1 g weighed amounts in polytetrafluoroethylene (PTFE) vessels. Material prepared in that way was subjected to microwave waves of 1400 W power and temperature of $200^{o}C$ for 40 minutes using the Multiwave 3000 Anton Paar mineraliser. The mineralised material and monthly collected samples of precipitation were subjected to chemical analysis for the content of selected metals (Al, Cd, Cr, Co, Cu, Fe, Ni, Pb, Zn), using the ICP-MS-TOF OptiMass 9500 mass spectrometer. Results consisted of an average value of three measurements. In order to control the quality of obtained results, such certified reference materials as ERM-CA713 made by the Institute for Reference Materials and Measurements in Belgium were used. The obtained data was statistically elaborated using the Statistica 13.1 program. Meteorological and climate data for the Kielce weather station was obtained from the OGIMET portal. The volume of emissions was elaborated basing on the data retrieved from the Regional Inspectorate of Environmental Protection in Kielce. Needle surface morphology was characterised by the method of scanning electron microscopy using a Hitachi TM3000 microscope (under full vacuum and with 15 kV accelerating voltage) at the Institute of Inorganic Chemistry and Technology at the Cracow University of Technology. The direction of air mass inflow was tested using the Hysplit model.

Results

The quality of atmospheric air in the Białe Zagłębie is primarily determined by the type of economy carried out in its area. The rock raw material mining and processing industry and, additionally, communal and living sector and road transportation are the largest sources of emissions there. Moreover, air masses from the Upper Silesian Industrial District and even the Czech Moravia, periodically occurring in the Białe Zagłębie and identified on the basis of NOAA Hysplit backward trajectories, may be an additional environmental burden (Fig. 3). The largest share of dust emissions to the atmosphere belonged to the Trzuskawica Lime Industry Plant located in the central part of the Białe Zagłębie, which emitted annually 131.7 Mg of dust, on average and the Lafarge Cement Plant in Małogoszcz, which emitted annually 129.75 Mg, on average in the years 2002–2018 (Fig. 2). During the analysed period, only the cement plant in Bukowa decreased its volume of emissions. In total, 263.3 Mg of dust from the plants monitored by the Provincial Inspectorate of Environmental Protection got into the atmosphere in 2016, 302.2 Mg in 2017, and 293.0 Mg in 2018. According to the regulation of the Minister of Environment (Journal of Laws of 2018, item 799), the permissible level of dust with a fraction of 10 microns - PM10 in the air is 50 $\mu g.m^{-3}$(daily average), and the limit of permissible exceedances during the year amounts to 35 days. The permissible annual PM10 level amounts to 40 $\mu g.m^{-3}$.

The analysis of suspended PM10 concentrations from the Provincial Inspectorate of Environmental Protection's station in the Białe Zagłębie, meteorological data and the NOAA Hysplit model showed that:

- the highest average annual PM10 concentrations were recorded in 2017, i.e. 85.3 $\mu g.m^{-3}$ for Nowiny and 35.8 $\mu g.m^{-3}$ for Małogoszcz,
- the biggest number of days with exceedances of the permissible level was recorded in 2017 in Nowiny, i.e. 198 days, in total,
- the values above the permissible level and the highest values were recorded for the cool half-year periods,
- the maximum value of PM10 concentrations at both stations (274.6 $\mu g.m^{-3}$ in Nowiny and 175.7 $\mu g.m^{-3}$ in Małogoszcz) fell on 8th and 9th January 2017, with such minimum temperatures on those days as:

-25.2 ^{o}C and − 26.3 ^{o}C, respectively,

- the maximum values of concentrations were recorded during the period of air inflow from the south-west direction, along with the lowest air temperature during the year.

Chemical analysis of dust samples from the Dyckerhoff Nowiny and Lafarge Małogoszcz cement plants showed a significant share of heavy metals in their composition (Table 1). The largest share was reported for iron and aluminium, lead and zinc (Table 1). The pH of both samples was alkaline, its value in H_2O and KCl was pH_{H2O} = 13.21 and pH_{KCl} = 13.02 for the sample from Małogoszcz and pH_{H2O} = 12.61 and pH_{KCl} = 12.38 for the sample from Nowiny.

Analysis of PM10 showed variable values throughout the year. Dust concentrations in the air correlate with the increase in cement and lime production (Fig. 4a). Increased values in winter periods could be related to the release of pollutants from domestic heating installations and the inflow of air from local and remote sources of industrial emissions [40], (Fig. 4b).

The hourly values of sulphur dioxide and nitrogen dioxide concentrations in the whole analysed period did not exceed the permissible values at both Provincial Inspectorate of Environmental Protection’s measuring stations. In the case of sulphur dioxide and PM10, there was an increase in pollution during the cold half-year and a decrease during the warm half-year with lower concentration values.

The relationship between SO_2 and PM10 concentrations and air temperature was noticeable (Fig. 5).

Based on the conducted research, it was found that the weighted average pH value of precipitation in 2016 was 5.91 (normal precipitation according to the classification by Jansen et al. [41]) with fluctuations from 5.30 (January 2016) to 6.57 (May 2016). Electrolytic conductivity (EC) was 4.50 mS.m^{-1} (significantly elevated). In 2017, the average pH value was 6.47 (slightly elevated) and conductivity – 7.12 mS.m^{-1} (extremely elevated). The lowest pH for precipitation was recorded in December 2017. In 2018, the slightly elevated pH (6.15) and extremely elevated electrolytic conductivity (9.95 mS.m^{-1}) were found. The lowest pH values were recorded in the winter months (January - pH 5.77, December - pH 5.39).

The analysis of heavy metal content showed the highest concentrations of iron, copper, aluminium and nickel in precipitation. Concentrations of other heavy metals did not exceed 100 µg.dm^{-3} in average monthly precipitation samples. The highest concentrations of iron in the monthly sample was found in January 2016 (580 µg.dm^{-3}). The highest concentrations for copper (180 µg.dm^{-3}) and aluminium (57.5 µg.dm^{-3}) were found, in turn, in September 2018. To compare to the entire study period, two months (January and September 2018) were distinguished due to elevated concentrations of all tested heavy metals. Such a situation could have been affected by the weather conditions. Low temperatures in January and February 2016 and the extremely dry summer of 2018 were favouring high concentrations of heavy metals in the air and their deposition, and after precipitation - due to leaching - were increasing their values in the analysed water samples. Statistically significant relationships ($p < 0.05$) were found among the individual elements being analysed, marked with an asterisk in Table 2.

High coefficients were accompanying Pb, Fe, Co and Al with all analysed heavy metals. The relationships of chromium with nickel and cadmium with copper were marked. The increased mineralisation (EC) could be associated with the presence of cadmium, copper, iron and aluminium.

Transplantation of lichens in the south-western part of the Świętokrzyskie Mountains indicated the accumulation of trace elements of anthropogenic origins. The amount of accumulated metals was calculated for each control point based on the difference between the concentrations of metals in the biota of lichens transplanted into the Białe Zagłębie and the concentrations of metals in the blank sample tested immediately after taking it from the Borecka Primeval Forest. The average content of accumulated heavy metals was the highest for aluminium (about 900 $mg.kg^{-1}$ d.m.) and iron over 400 $mg.kg^{-1}$ d.m.; and, both elements reached the highest concentrations during the third series of transplantation. The lowest concentrations of aluminium in the lichen thallus were recorded during the fourth series of transplantation (325.6 $mg.kg^{-1}$ d.m.), while for iron - during the first series (222.6 $mg.kg^{-1}$ d.m.). The highest concentrations of these metals were observed in Bolechowice (11), Bukowa (13) and Lipowica (21), located in the immediate vicinity of the cement plant [22]. The increased content of iron and aluminium in the air, apart from the emission from cement plants, was also associated with the weathering process of rocks and minerals [42]. The next largest element in the six-month series was zinc. Its values were the highest during the second series of transplantation, with an average of 41.7 $mg.kg^{-1}$ d.m. The highest concentrations were recorded in thalli exposed in Bolechowice (11) and Lipowica (21), and the lowest ones were found in Chorężów (7) (in three series below 5 $mg.kg^{-1}$ d.m.). Copper and lead concentrations in lichen were similar to each other in all analysed periods. Visible differences occurred during the fourth series in which an average of 12.7 $mg.kg^{-1}$ d.m. was recorded for lead and 19.56 $mg.kg^{-1}$ d.m. - for copper (Fig. 6). The highest concentrations of lead (up to 64 $mg.kg^{-1}$ d.m.) were recorded for the lichen samples from Bolechowice (11) and Lipowica (21), while the highest ones of copper (up to 56 $mg.kg^{-1}$ d.m.) were found in the samples collected from Jaworznia (1), Wymysłów (22), Brzeziny (17), and Milechowy (6).

Chromium, cobalt, cadmium and nickel concentrations in all exposure series did not exceed 1 $mg.kg^{-1}$ d.m. During the first year of research, there was a noticeable increase in the accumulation of the analysed elements for the cold half-year in comparison with their accumulation in the warm half-year. It was the largest for zinc - by 50%, lead and copper by 23%, aluminium by 17%, and iron and nickel by 10%. Only concentrations of cobalt, chromium and cadmium slightly decreased. During the second year of lichen transplantation, the concentrations of accumulated elements were higher in the samples exposed in the cold half-year in comparison with the elements accumulated in the warm half-year for: copper (by 83%), cadmium (by 64%), lead (by 57%), cobalt (by 54%), and chromium (by 51%). A decrease in concentrations was noted for other heavy metals. It was the highest for aluminium (by 174%), zinc (by 97%), iron (by 50%), and nickel (by 9%).

Needle pH determinations showed the average values of pH_{H2O} 5.62 and pH_{KCl} 5.28. The highest values of pH_{H2O} 6.38 and pH_{KCl} 5.81 were recorded in the central part of the study area, i.e. in Polichno (15).

Average content of the analysed metals in the samples of needles was the highest in the case of aluminium (over 400 $mg.kg^{-1}$ d.m.), iron (270 $mg.kg^{-1}$ d.m.) and zinc (65 $mg.kg^{-1}$ d.m.). The content of lead, copper, nickel and strontium did not exceed 10 $mg.kg^{-1}$ d.m. The content of iron and aluminium found in the air, apart from the emission from cement plants, was also associated with the weathering process of rocks and minerals [42]. In 2018, pine needle samples for physico-chemical and chemical tests were collected again. The analysis of results showed a significant increase in heavy metal concentrations, especially for chromium (3.3-fold), aluminium (3-fold), manganese (2-fold), and nickel (1.4-fold), compared to the samples from 2016. Other heavy metals (lead, copper, cobalt, zinc, strontium, and iron) had a similar level as that in the previous study period. Considering the small changes in the volume of emissions, the fact of increased concentrations should be associated with favourable conditions for deposition of dust on pine needles (high air temperature, low annual precipitation). Depending on the location, and above all, the distance from the emitter, the volume of accumulated elements by the pine needles varied considerably; while the highest concentrations of lead, zinc, chrome, iron, aluminium and copper were recorded in the control sites located within 5 km from the industrial plants and nearby quarries (Fig. 7).

There was a spatial pattern of concentrations of selected trace elements (Pb, Cu, Ni) observed in a latitudinal system, i.e. higher in the area of lime and cement plants within 2 km from the emission source, and lower east of them, located in the vicinity of forest complexes within more than 2 km from rock processing plants. A source of heavy metals in the vicinity of lime plants in Bukowa may be the co-combustion of car tires in a process of lime production. Particles deposited inside the inter-cellular structure of needle may penetrate it and thus cause its capping which disturbs a gas exchange [43, 44, 45]. SEM/EDS analysis of the chemical composition confirmed the presence of metals (Pb, Fe and Al) as well as Ca, K and Mg (Fig. 8). The most important elements included in the cement-lime dust comprise of Pb, Fe, Al, and Ca. It may therefore be concluded that the direct source of emissions of elements found on the surface of the needles were the cement and lime plants operating in the study area.

Using the PCA (principal component analysis) method, three main components were distinguished, i.e. PC1 – PC3 (Table 3). In total, they generated 64% of cumulative total variance of trace elements in the samples from the analysed area of the Białe Zagłębie, regardless of bio-indicator's location. They take into account the conditions associated with the cement and lime industry operating in this area (PC1-PC3) and transportation resulting from the course of the S7 express way at a distance of about 1 km from the study area (PC3).

The first component (PC1) generated 34% of total variance and showed high weight ($\leq$ -0.87) for Fe and Pb (Table 3). The second component (PC2), in turn, formed 17% of total variance with the highest weight for Zn and Cr. Also important is the PC3 analysis (13% of variance) which indicated high weight for Cu (Fig. 9).

Discussion Of Results

As a result of local emissions, the chemical composition mainly showed the impact of dust pollution, confirmed by the presence of heavy metals, especially lead, chromium, nickel, and copper. The results of the chemical composition of precipitation on the Malik Mountain were similar to the concentrations of nickel, cadmium, cobalt, and chromium obtained on the basis of atmospheric precipitation in the region of Upper Silesia [46]. In all years of research, the average annual concentrations of iron and copper in the precipitation water from the Białe Zagłębie were several times higher than those obtained in the most industrialised and urbanised part of the Central Europe. Much lower concentrations of the analysed metals were found in atmospheric precipitation studied in 2007-2008 in the Tibetan Highland at Nam Co [47]. In samples of the melted mountain glacier from Mount Everest [48] and in snow samples taken in the Himalayas [49] and the Pamir Mountains [50], lower concentrations of aluminium, chromium, iron, and cobalt were found than in the Świętokrzyskie Mountains. Only concentrations of lead, aluminum and cobalt in the urban part of Mersin in Turkey [51] were several times higher than in the south-western part of the Świętokrzyskie Mountains. Research conducted in Singapore [52], Virginia [53], Nakanoto [54], and the Aegean Sea [55] showed similar concentrations of lead, cadmium and chromium to those found in the Świętokrzyskie Mountains. Monthly average copper concentrations on the Malik Mountain, only in the case of research in 2017, especially for February and March, were comparable with the results obtained in precipitation water in Singapore [52]. In other regions of the world, lower copper concentrations were recorded than in the Świętokrzyskie Mountains (the lowest ones in the Himalayas and Virginia).

Research using the same lichen species is carried out in many regions of the world. Due to their high accumulation capacity, they are widely used in areas exposed to high industrial pressure. In Poland, studies on the same species were carried out by Białońska and Dayan [56] in the same transplant periods. Lead and zinc concentrations had been two times higher (except for Bukowno), cadmium concentrations had been 10 times higher; nickel, copper and iron concentrations had been at a similar level; and chromium concentrations had been lower by half (except for Alwernia) than the metal concentrations recorded for the lichens. Studies conducted by Sawicka-Kapusta et al. [16] as part of the Integrated Environmental Monitoring (IEM) in Poland in 2010, had conducted lichen-indication studies of Hypogymnia physodes occurring in its natural environment (in situ) in the IEM study base stations. The obtained metal concentrations were close to the values found in the lichen thalli in “Białe Zagłębie" in the case of iron and copper, and several times higher in the case of cadmium and zinc. In the Kalingrad Oblast (Russia), Koroleva and Revunkov [57] studying metals in the in the *Hypogymnia physodes* (L.) Nyl. found similar concentrations of copper, lead, nickel and strontium, as well as twice as high zinc concentrations and three times higher iron concentrations than those recorded for the control points. Studies conducted by Poličnik et al. [37] in Slovenia and Mikhailova et al. [36] in Russia with the annual exposure period of the same species of transplanted lichen, had indicated varying accumulation of Fe, Pb, Cu, Cd and Zn throughout the year. Lichen transplantation carried out by Asplund et al. [58] proves that it can be used to estimate the dependence of the impact of selected tree species on the local chemical environment. After a 1 year transplantation onto trunks, lichens on beech had significantly higher concentrations of base cations (Ca, Mg, K), lower Mn, Zn, and had similar Al, Fe concentrations.

Studies carried out on pine needles taken from the forests of the north-western part of Poland [59], characterised by the lack of significant impact of industrial pressure on air quality, showed significantly lower concentrations of iron (34 $mg \cdot kg^{-1}$ d.m.), zinc (48 $mg \cdot kg^{-1}$ d.m.), copper (3 $mg \cdot kg^{-1}$ d.m.) and chromium (1 $mg \cdot kg^{-1}$ d.m.). Studies conducted in Słupsk in the northern part of Poland [18] showed similar concentrations of zinc in washed needles to those in the study area, with a mean value of 66.8 $mg \cdot kg^{-1}$ d.m., and significantly higher concentrations in the case of lead, amounting to 13.3 $mg \cdot kg^{-1}$ d.m. In Olsztyn, in turn, located in the north-eastern part of Poland, considered as the area with the lowest anthropopression [60], concentrations of lead in pine needles were almost 9 times lower (0.13 $mg \cdot kg^{-1}$ d.m.) and - in the case of chromium - 8 times lower (0.03 $mg \cdot kg^{-1}$ d.m.) than in the study area. Concentrations of lead and zinc found in pine needles in the Upper Silesian conurbation, being the most industrialised part of Poland, reached a few hundred higher level [61] than in the study area. Studies conducted on the Kola Peninsula (Russia), in its industrialised part [62], showed comparable concentrations of chromium and zinc and much higher concentrations of lead (7.4 times), strontium (2 times), copper (8.6 times), nickel (63.4 times) and iron (3 times) than in the study area. In the northern part of Estonia, being exposed to alkalisation by the cement plant [63,17], concentrations of chromium, lead, iron, zinc and copper were found to be about half as high as in the study area, but it should be noted that the authors did research on one-year-old needles. Studies conducted by Juranović-Cindrić et al. [64] confirm the physiological changes of needles by demonstrating the relationship between mineral deficiency in soils and advanced alkalisation. Studies carried out by Barga-Wiecławska et al. [21] in the Białe Zagłębie confirm the changes in the soil profile towards alkalisation resulting from more than forty-year-old emission of cement-lime dust.

The conducted principal component analysis indicated the conditions associated with the cement and lime industry operating in this area (PC1-PC3) and transportation resulting from the course of the S7 express way at a distance of about 1 km from the study area (PC3). The Kozłowski's research (2013) showed that the cement and lime dust emitted by the industry operating in this area is characterised by an increased content of Fe, Pb, Cr, Zn, and Cu resulting from the technological process used. For the production of clinker and lime, coal, coal dust, coke and car tires are commonly used.

Conclusions

The aim to assess the extent of the impact of air pollution sources on the environment is a difficult task, especially if there are many emitters located in a small area. Such a case is in the south-western part of the Świętokrzyskie Mountains, where several plants extracting rock raw materials and producing cement and lime have been located in close proximity to each other. This area already in the 1970's was classified as the area of the so-called ecological disaster.

Based on the conducted research, significant changes in the natural environment were found in the Białe Zagłębie. They mainly concern the air quality and atmospheric precipitation properties which in turn affect the entire natural environment and people. The analysis of air research showed significant dynamics of the amount of air pollution in individual years. A large number of days with exceedances of the permissible PM10 concentrations at both measuring stations in Nowiny and Małogoszcz should be noted, as well. A relationship between air temperature and dust concentrations during the periods of severe frosts was found. Such a situation causes an additional reduction in the air quality in connection with emissions from the communal sector (low emission).

The research carried out on the geo-indicators has confirmed the impact of existing plants in the Białe Zagłębie on the quality of atmospheric precipitation. It was discovered that both the physico-chemical properties and chemical composition of precipitation are subject to transformation. An increase in the natural pH, electrolytic conductivity and the presence of heavy metals of anthropogenic origins, i.e. lead, zinc, cadmium and chromium were found. Increased pH and mineralisation values indicate anthropogenic pressure related to the cement and lime industry branch dominating in the region and remote sources of emissions. The concentrations of heavy metals, especially iron, aluminium, manganese, and zinc occurring in all measuring points indicate a significant dispersion of pollutants in the atmosphere and the possibility of further movement.

Lichens transplanted to the study area accumulated the largest amount of heavy metals among the analysed indicators. Four measurement series conducted in the half-year periods showed a variable accumulation of elements, higher in the cool half-year, and lower in the warm half-year. The most important factor affecting the volume of accumulated metals was the distance from the source of emissions (industrial plant, fast highways), i.e. the closer the distance, the higher the heavy metal content was in the bio-indicator. Local orographic barriers in the form of hills and dense forest complexes were disturbing the dispersion of pollutants in the atmosphere and caused variable accumulation in the thalli of bio-indicators. The lichens exposed in the Białe Zagłębie accumulated significant volumes of the analysed trace elements, exceeding the concentrations occurring in the Borecka Primeval Forest several times (Cu – 4.2 times, Pb – 2.9 times, Cr – 2.8 times, Ni – 2.1 times, Fe – 1.8 times).

The collected pine needle samples indicated physico-chemical and chemical properties conditioned by the deposition of cement and lime dust. The highest concentrations of heavy metals were found in those samples which were collected up to 2 km from the cement plants in Nowiny and Małogoszcz (Cr, Co, Cu, Ni) and the lime plants in Trzuskawica and Bukowa (Zn, Sr, Pb). Studies on the content of selected trace elements confirmed the difference between the samples of unwashed and washed needles (the largest for Fe, Al, Zn), which resulted from deposition of dust from the atmosphere and their deposition on the surface of pine needles.

Analyses, including SEM photomicrographs, confirmed the effectiveness of capturing cement and lime dust, along with heavy metals, by coniferous forest complexes within the area of Białe Zagłębie. In addition, it may be noted that fine dusts, regardless of their chemical composition, adversely affect the stomata, which may lead to gas exchange reduction. As a consequence, the reduction of gas exchange may lead to a decrease in the efficiency of photosynthesis and thus limit the development of the analysed forest stand. Considering the slight changes in the volume of emissions from the cement and lime plants being monitored, the fact that the concentrations of heavy metals in the pine needles from 2018 increased in comparison with the samples from 2016 should be associated with a significant change in meteorological conditions. The year 2018 was extremely dry and warm, and that certainly enabled dust deposition and was effectively making it difficult to flush it from the surface of needles.

The statistical method used for the main components of PCA showed a significant impact of the industry functioning in the analysed area.

The geo- and bio-indicators used in the research are used to assess the state of the natural environment under the influence of anthropogenic pressure in a given study area. High sensitivity to pollution and accumulation capacity allowed for delimitation of the zone most exposed to the impact of the cement and lime plants. Chemical composition of precipitation, pine needles and transplanted lichens were conditioned by deposition of cement and lime dust from the industrial plants and quarries located in the study area.

Abbreviations

PCA: Principal component analysis; EC: electrolytic conductivity; SEM: Scanning electron microscope; EDS: Energy dispersive X-ray spectroscopy; ICP-MS-TOF: Inductively Coupled Plasma- Mass Spectrometer- Time-of-Flight; d.m.: dray mass; Mg: megagram; PTFE: polytetrafluoroethylene.

Declarations

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Declarations

The authors report no applicable declarations during this manuscript.

Authors' contributions

MSz was involved in the sampling and experiments. MSz wrote the manuscript. RK designed the study. WŻ made SEM/EDS analysis. All authors read and approved the final manuscript.

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Availability of data and materials

The datasets obtained and analyzed during the current study are available from the corresponding author on reasonable request.

Ethics approval and consent to participate

Not applicable.

Consent for publication

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Competing interests

The authors declare that they have no competing interests.

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Tables

Table 1. Chemical analysis of selected dust components from cement plant in Białe Zagłebie [14]

Cement plant	Pb	Cd	Cr	Co	Cu	Ni	Zn	Al	Fe
	mg·kg^{-1} d.m. (dry mass)								
Małogoszcz	38.0	0.4	0.7	0.4	1.4	3.7	19.8	1760.0	365.0
Nowiny	3139.0	41.4	4.2	1.2	6.8	8.5	1373.1	4280.0	588.0

Table 2. Correlations of selected physico-chemical and chemical properties of precipitation. Determined correlation coefficients were significant ($p < 0.05$)

Variable	Pb	Cd	Cr	Co	Cu	Ni	Al	Fe	pH	EC
Pb										
Cd	**0.576**									
Cr	**0.384**	-0.171								
Co	**0.411**	0.302	**0.501**							
Cu	**0.645**	**0.721**	0.106	**0.404**						
Ni	0.203	-0.055	**0.705**	**0.857**	0.140					
Al	**0.767**	**0.805**	0.108	**0.445**	**0.914**	0.152				
Fe	**0.512**	**0.479**	**0.484**	**0.823**	**0.690**	**0.712**	**0.670**			
pH	-0.193	-0.130	-0.328	-0.302	-0.073	-0.286	-0.167	-0.119		
EC	0.257	**0.496**	-0.095	0.254	**0.549**	-0.053	**0.516**	**0.446**	0.041	

Table 3. PCA analyses of heavy metals

Variable	Component		
	PC1	PC2	PC3
Pb	-0.824*	-0.210	0.115
Cd	-0.514	0.563	-0.254
Cr	0.079	-0.776*	-0.350
Co	-0.590	-.0146	0.384
Cu	-0.240	0.341	-0.746
Ni	-.0641	0.015	-0.077
Zn	-0.451	-0.662*	-0.292
Al	-0.589	0.059	0.415
Fe	-0.870*	0.093	-0.117
% of variance	34	17	13
% in total	34	51	64

* PC1 ≤ -0.9; PC2-PC3 ≥ 0.6

Figures

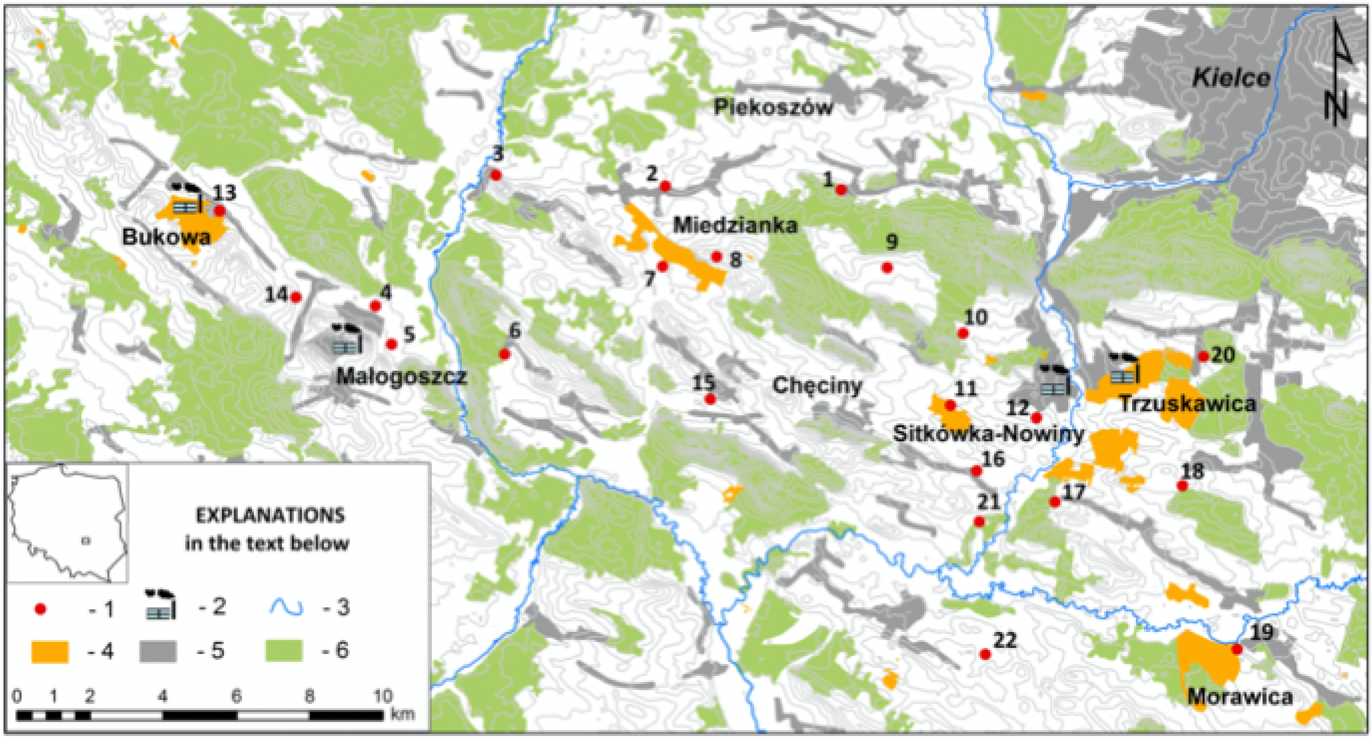

Figure 1

Location of study area (elaborated by M. Szwed on the basis of BDOT and CORINE L and Cover v.2012), 1- sampling points, 2 - cement and limestone plants, 3- rivers, 4 - quarries, 5 - buildings, 6 - forests

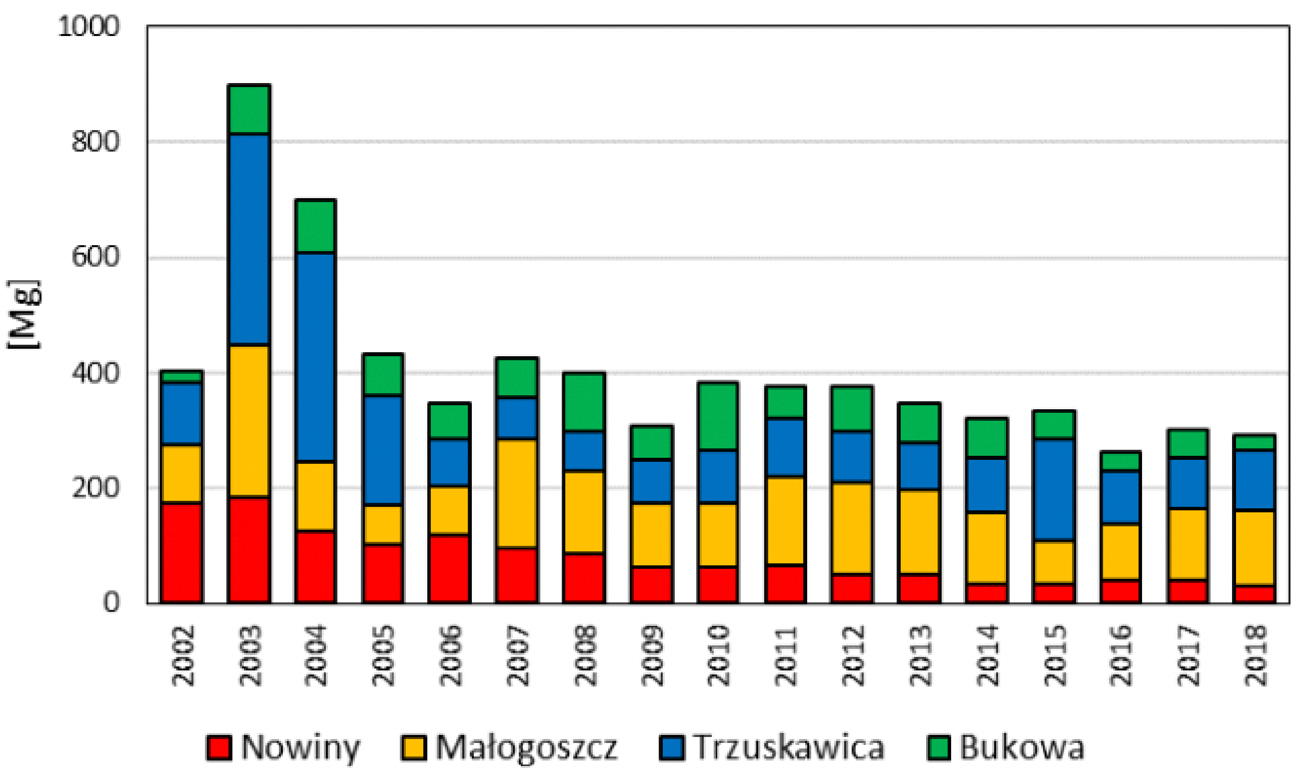

Figure 2

Volume of cement and lime dust emissions in the Białe Zagłębie in the years 2002-2018 (data by Provincial Inspectorate of Environmental Protection in Kielce)

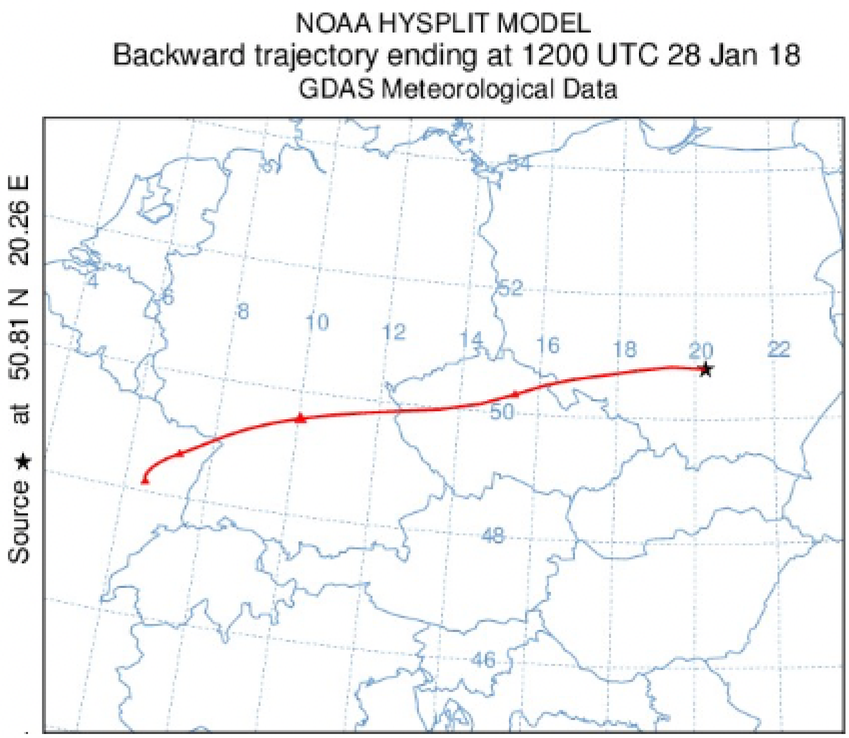

Figure 3

Backward trajectory graph for Nowiny determined on days of highest PM10 concentrations in the atmospheric air, using the Hysplit model

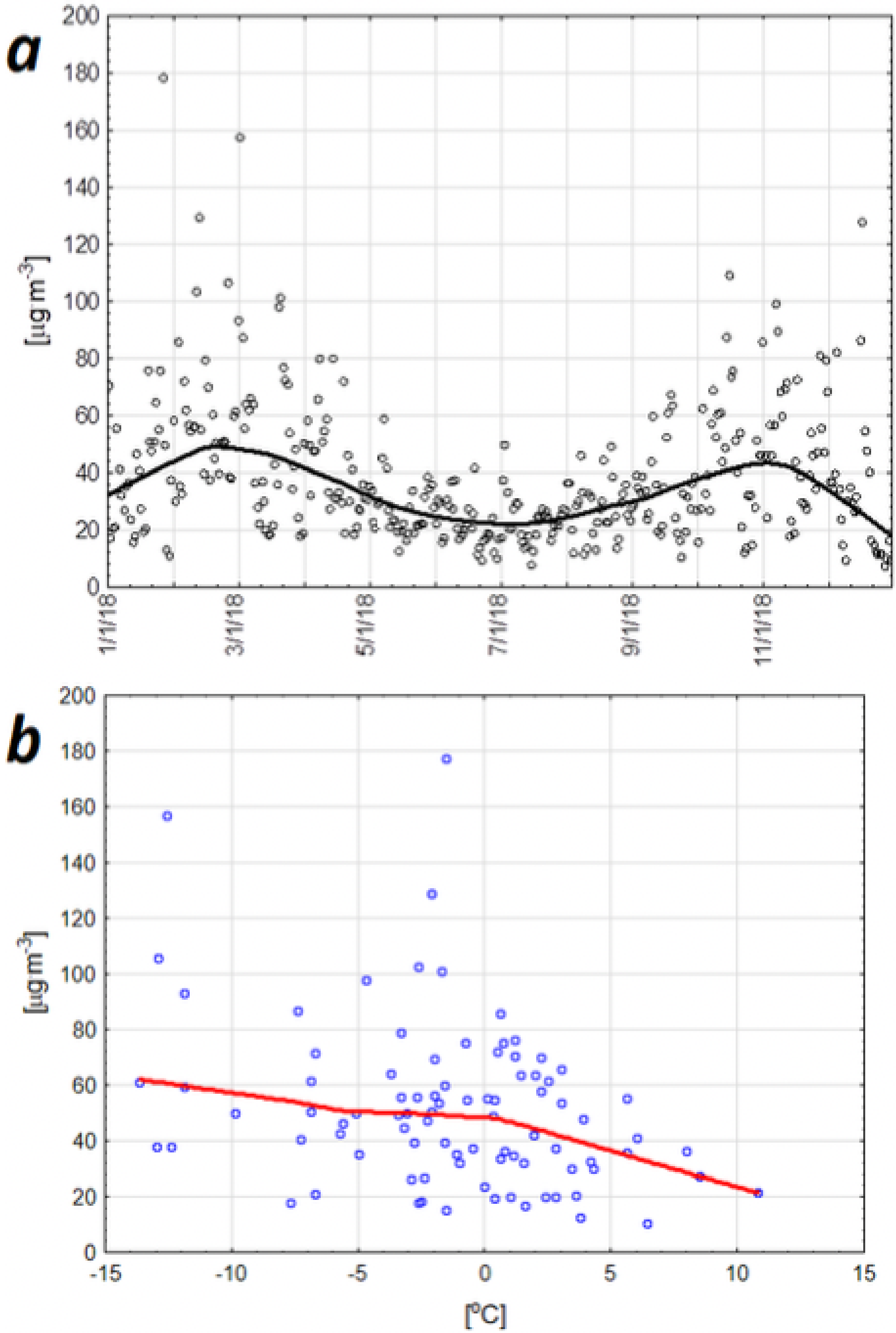

Figure 4

PM10 concentrations in Nowiny, a – for a year, b – for winter period – as a function of the air temperature

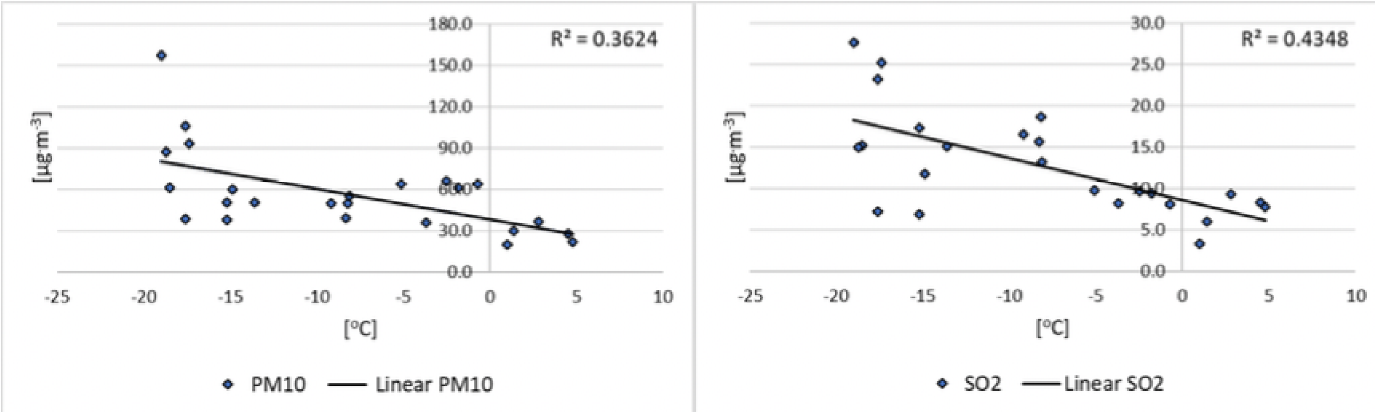

Figure 5

Relationship between SO2 and PM10 concentrations and air temperature (January 2018).

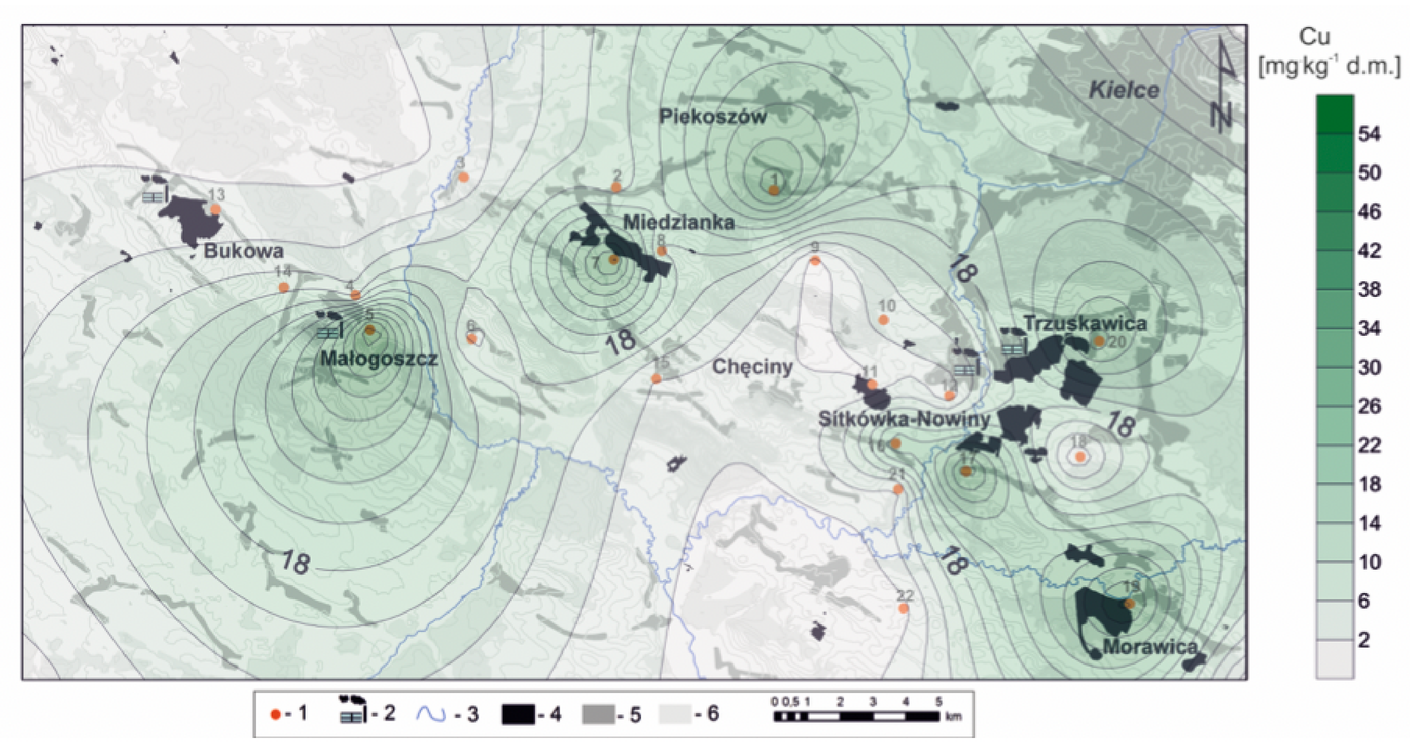

Figure 6

Copper concentrations in transplanted lichen - fourth series. (Legend: 1- sampling points, 2 - cement and limestone plants, 3 - rivers, 4 - quarries, 5 - buildings, 6 – forests)

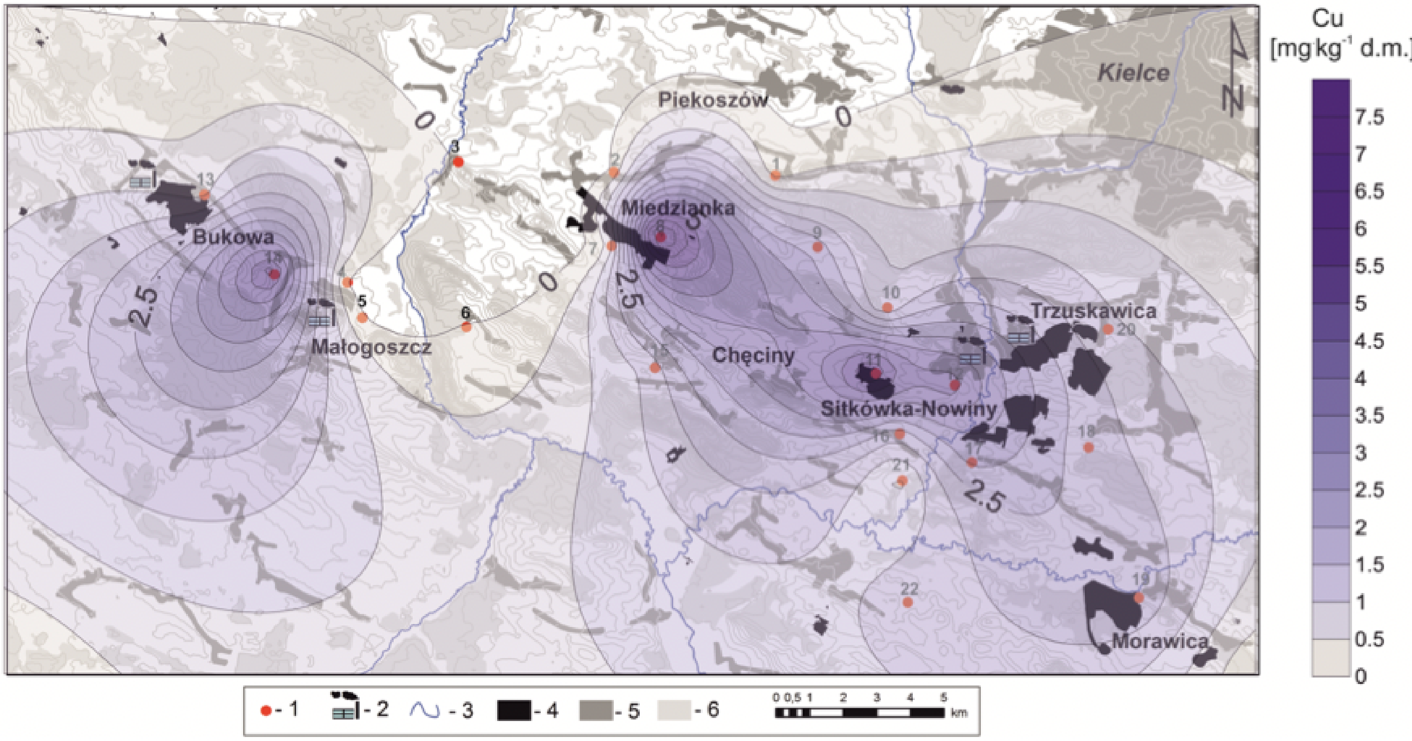

Figure 7

Copper concentrations in pine needles - second series. (Legend: 1- sampling points, 2 - cement and limestone plants, 3 - rivers, 4 - quarries, 5 - buildings, 6 – forests)

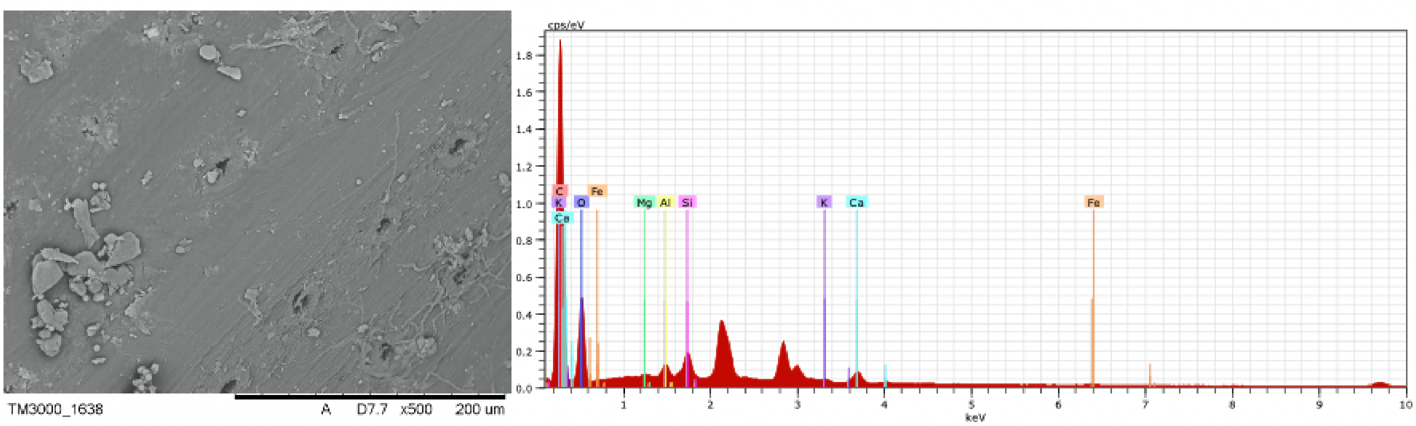

Figure 8

SEM image and EDS analysis of the needles’ surface - collected in the near vicinity of the Trzuskawica Lime Industry Plant in Kowala

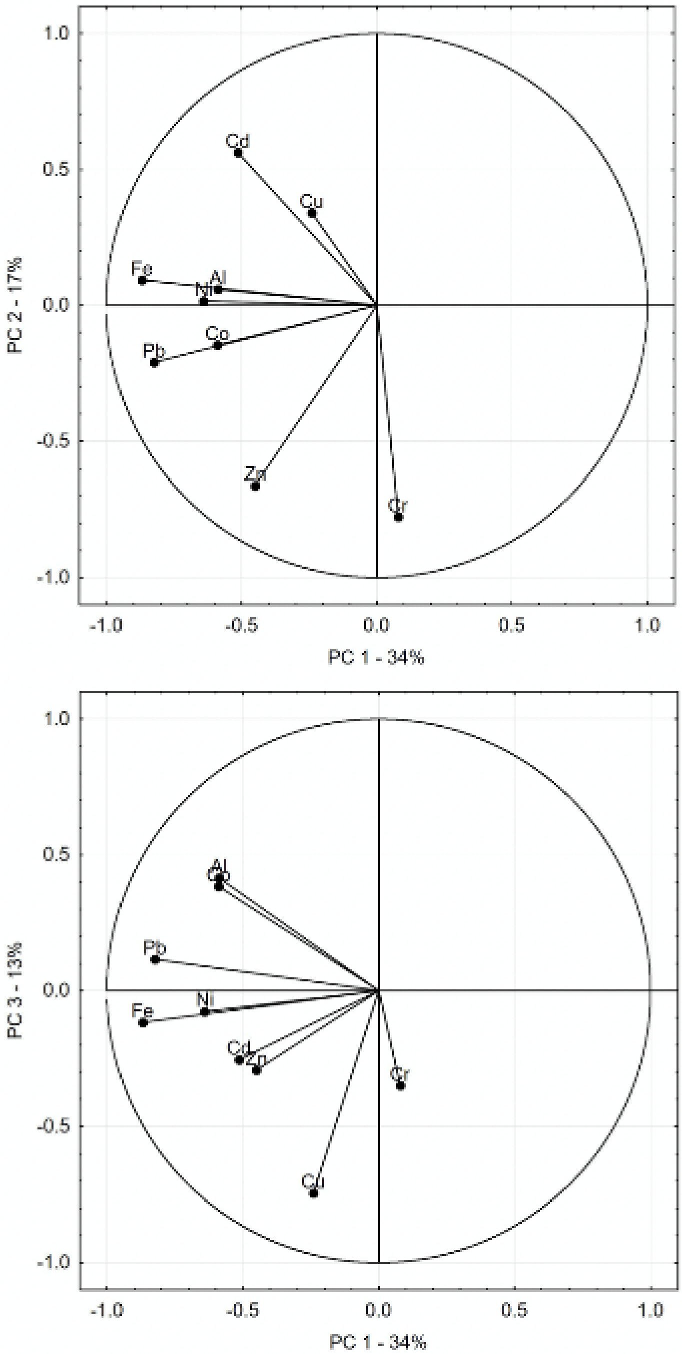

Figure 9

Graphic image of relationships among PC1, PC2 and PC3 components